

WASTES INTO PRODUCTION

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STRUCTURE AND PROPERTIES OF COMPOSITE SILICATE MATERIALS BASED ON ELECTRO-CORUNDUM — NIOBIUM PRODUCTION SLAG

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The properties of composite silicate materials (CSM) based on electro-corundum, which is byproduct of electrometallurgical production of niobium, are presented. A scheme for heat-treatment of CSM is proposed. The CSM compositions developed are recommended for protecting equipment used in the chemical industry.

Key words: composite silicate materials, electro-corundum, niobium production slag, refractory clay.

New chemically stable composite silicate materials (CSM) can be developed by means of highly efficient modern technology based on drawing technogenic wastes from aluminum-thermal processes of the metallurgy of rare elements into complex processing.

The connectedness of the glass-forming aluminum-silicon-oxygen framework of refractory silicate components depends on the conditions of heat-treatment. Usually, the chemical production equipment being protected operates not only under high corrosion-erosion wear conditions but also at high temperatures. For this reason the behavior of the recommended coatings in wide temperature intervals was studied.

Chemically stable CSM compositions, where pre-melted aluminum oxide (electro-corundum) is used as filler, possess a number of unique properties. The slag waste used in the present work — remelted aluminum oxide, the high-temperature α -phase of Al_2O_3 (corundum) with inclusions of metallic niobium particles — is a valuable raw material which has undergone preliminary mechanical and heat treatment. Previously, ceramic mix compositions with refractory clay additions were used to obtain acid-resisting building materials [1, 2].

The optimal compositions of ceramic mix, which contain refractory clay, slag from the industrial processes, liquid

glass and sodium silicofluoride are presented in Table 1. The content of the components is as follows (wt.%): 20.0 – 30.0% liquid glass, 5 – 10% refractory clay (≤ 0.5 mm fractions), 65.0 – 70.0% electro-corundum (< 1 mm fractions), and 3.4 – 5.1% sodium silicofluoride. A ceramic mix with content of electro-corundum, refractory clay, liquid glass and sodium silicofluoride (introduced to accelerate solidification) in precisely these ratios makes it possible to obtain with subsequent annealing at 1100 °C material with high strength and heat and chemical resistance (in sulfuric and hydrochloric acids and in alkaline solutions) and low water absorption.

The main physical-technical properties of optimal CSM samples are presented in Table 2 [3].

TABLE 1. Optimal Compositions of Ceramic Mix

Sample	Content, wt.%			
	Electro-corundum*	Refractory clay	Liquid glass	Na_2SiF_6 ** (excess of 100%)
CSMcl.-1	65	5	30	5.1
CSMcl.-2	66	6	28	4.7
CSMcl.-3	67	7	26	4.4
CSMcl.-4	68	8	24	4.0
CSMcl.-5	69	9	22	3.7
CSMcl.-6	70	10	20	3.4

* The granulometric composition of electro-corundum is: 0.05 – 0.4 mm — 50%; 0.1 – 0.1 mm — 50%.

** Comprises 17% of the mass of liquid glass.

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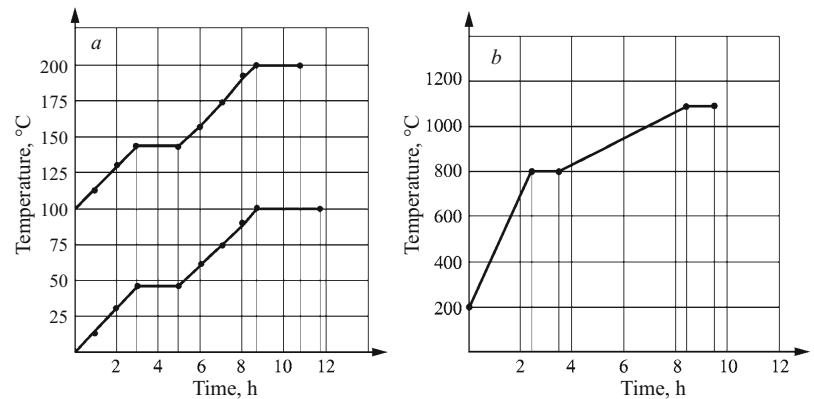


Fig. 1. Heat-treatment regime for composite materials: *a*) heat-treatment to 200°C; *b*) same, from 200 to 1100°C.

In contrast to β - Al_2O_3 which possesses a structurally defective, incomplete crystal lattice, i.e., with unoccupied structural sites, α - Al_2O_3 possesses a strong, completed, crystal lattice. Heat-treatment of CSM is done at temperatures no higher than 1100°C (established experimentally), since all physical-chemical processes are completed at this temperature and for this reason no transformations occur in the structure of the composite material.

I. I. Kitaigorodskii, et al. [4] recommend raising the temperature slowly to 100°C, since dehydration of the green material and reaction between the sodium silicofluoride and liquid glass is completed at 1100°C. Slowly raising the temperature to 200°C is recommended in [5]; the authors of [6] indicate that NaO forms at 500 – 600°C and NaF at 1210°C, which in turn destroys the Al_2O_3 lattice. G. I. Knigina, et al. [7] recommend the following temperature rise regimes: to 200°C — ≤ 2 K/min; 200 – 800°C — from 4 to 60 K/min; above 800°C — ≤ 1.5 K/min.

In the CSM developed intense dehydration processes occur in the temperature interval 25 – 200°C, and subsequently to 480 – 520°C the residual moisture is removed and sin-

tering processes begin. Chemical transformation processes are completed at 850°C, and subsequent temperature rise to 1100°C results in sintering of the material, which additionally simplifies its structure. Thermal analysis also confirms the data presented. The optimal heat-treatment regime for CSM has been developed taking into consideration the thermal conditions in different chemical plants and on the basis of thermographic studies (Fig. 1). According to the plot, the total heat-treatment time for composite materials is 31 h 10 min [8].

Figure 2 shows photomicrographs of heat-treated samples, where petrographic analysis shows the structure of all samples to be essentially a glass ceramic phase. Mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ is an embryo in the samples CSMcl.-2, -4 (CSMcl. — composite silicate materials with clay additions), which directly influences the physical-chemical properties of the synthesized materials. Crystallization of this material in the structure of the samples is accompanied by considerable densification and hardening of the ceramic paste, which largely determines chemical and thermal resistance to alumi-

TABLE 2. Properties of Samples without Heat-Treatment and Annealed at Temperature 1100°C

Sample	Shrinkage in air, %	Density in air-dried state, g/cm ³	Apparent porosity, %	Density, g/m ³	Wearability, g/cm ²	Bonding strength, MPa	Water absorption, %	Thermal conductivity, W/(m · K)	Heat-resistance, number of thermal cycles 800°C – water (5 – 25°C)		Strength, MPa	
									before crack appearance	before fracture	compressive	bending
CSM-2	0.1	1.56	7.0	2.9	0.01	0.5	4.3	6.4	15	21	75.2	9.7
CSM-9	0.1	1.52	7.1	2.8	0.01	0.6	5.2	6.6	15	20	80.7	11.7
CSM-14	0.1	1.51	7.2	2.8	0.01	0.5	5.4	6.7	15	21	81.2	13.2
CSMcl.-1	0.3	1.45	6.9	3.0	0.03	0.5	5.0	6.9	18	22	102	14
CSMcl.-2	0.3	1.41	6.9	3.1	0.02	0.5	5.3	6.8	19	23	102	14
CSMcl.-3	0.4	1.41	7.0	3.1	0.02	0.5	4.5	6.9	17	22	104	14
CSMcl.-4	0.4	1.45	7.0	3.1	0.01	0.5	5.2	6.9	18	22	105	15
CSMcl.-5	0.5	1.47	6.9	3.2	0.01	0.5	5.0	6.9	19	24	110	16
CSMcl.-6	0.6	1.60	6.9	3.2	0.01	0.5	4.5	6.9	19	24	110	16

* With St3 steel.

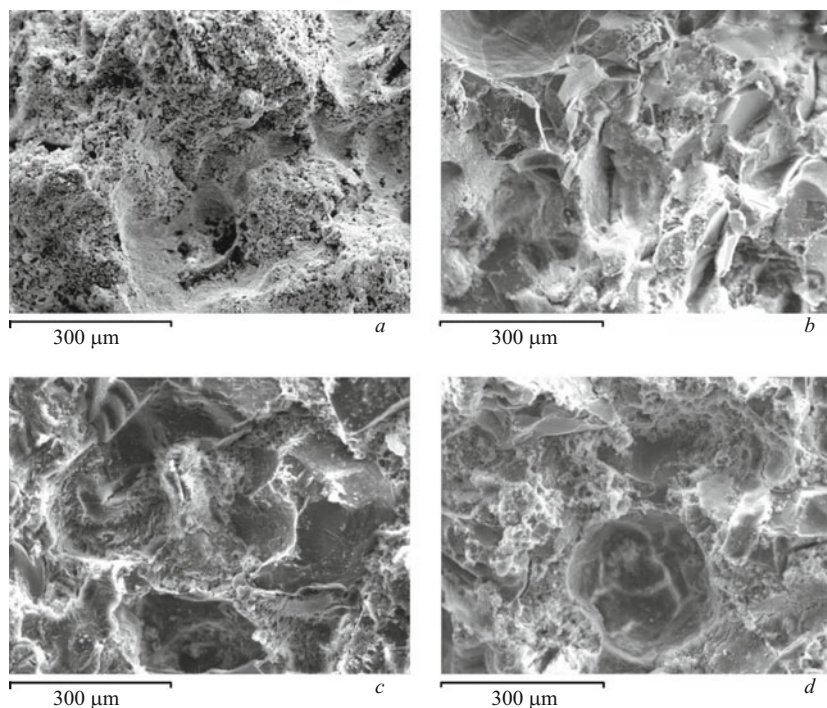


Fig. 2. Photomicrographs of CSM: a) CSM-4; b) CSM-9; c) CSMcl.-2; d) CSMcl.-4.

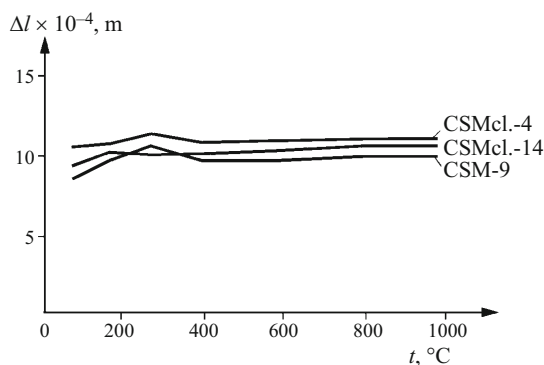


Fig. 3. Temperature dependence of the relative elongation Δl of CSM.

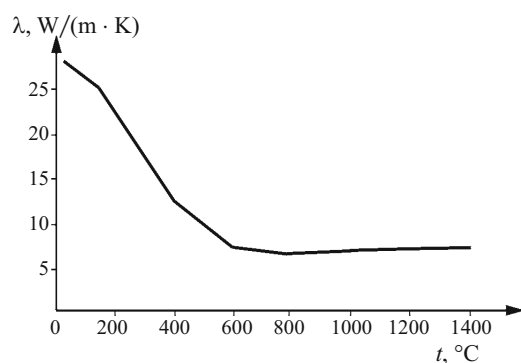


Fig. 4. Temperature dependence of the thermal conductivity λ of CSM.

num-silicate glass ceramic materials. The developed fracturing and porosity increase thermal stability.

A distinguishing feature of CSMcl. microstructures is direct convergence of large grains, forming a real contact at points of contact, which develops during annealing of the material with formation of a strongly bound structural framework. During heat-treatment large grains sinter and fine clay partially bakes to large grains of electro-corundum, sintering autonomously. Sintering of large grains, which occurs predominantly by surface diffusion, occurs with practically no shrinkage. Because of the stiffness of the structure formed by the large grains, sintering of the clay has no effect on the shrinkage of the entire system. The total volume and porosity of the system remain practically unchanged. Only partial redistribution of matter in the volume of the pressed material and the relative increase of the closed porosity owing to pore formation during sintering of the fine fraction of the clay and electro-corundum is possible.

A portion of the fine grains of electro-corundum and clay, which is in direct contact with the surfaces of large grains of electro-corundum, becomes baked to these surfaces and is absorbed by large grains in the process of recrystallization. Different stages of baking and recrystallization are clearly seen in the figures presented.

One of the most important properties of CSM was also investigated — thermal expansion, on which depends the temperature interval where the compositions reliably protect equipment and CSM are compatible with the surface coating of equipment. Incompatibility of the linear thermal expansion coefficient (CLTE) can lead to cracking and separation of the protective coating irrespective of the chemical resistance and mechanical strength. Studies of the CLTE of the CSM developed showed that these values coincide with the CLTE of St3 steel; this confirms that the coatings indicated can be used on metal surfaces. The relative elongation of the CSM samples at temperatures to 1000°C is shown in Fig. 3.

The dependence presented is strictly linear. This indicates that virtually no transformations occurred during heating. The average value of the CLTE of the proposed CSM in the temperature interval 20 – 1000°C is $10.5 \times 10^{-6} \text{ K}^{-1}$. In heat treatment, the small difference of the CLTEs of steel and CSM (the CSM CLTE is somewhat lower than that of steel) improves adhesion (bonding) of CSM to steel; the bonding strength is 0.5 – 0.6.

Figure 4 shows the temperature dependence of the thermal conductivity of CSM. Evidently, the thermal conductivity of the compositions is negligible at high temperatures. This increases the prospects for using the new compositions at high temperatures.

In summary, the structure and, correspondingly, the properties of CSM are determined by the optimal composition of the coarse and fine fractions of electro-corundum, and in CSMcl. by the fine clay fraction also. The recommended compositions of CSM can be used successfully to protect equipment used in the chemical industry.

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